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INTERNAL COORDINATES FOR THE H^+ - H PROBLEM

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ABSTRACT

Three translational and three rotational degrees of freedom are separated from the Schroedinger equation for H^+- H . The separation of the rotational degrees of freedom is carried out using two different definitions of the "body-fixed" axes. The resulting exact equations involve only the coordinates of the internal motion of the three particles, and are symmetric under the interchange of the two protons. Three different sets of internal coordinates are considered for each of two specifications of the standard configuration, or body fixed axes.

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The potential energy of a system of N particles moving in free space, is invariant under a translation of the center of mass of the entire system. This commutativity of the hamiltonian of the system with the translation operator implies the conservation of the total linear momentum and enables one to write the total wave function as a product of functions which describe the motion of the center of mass and that of the system relative to the center of mass.

Moreover, in field-free space, the potential, and therefore the hamiltonian of relative motion, is invariant under the continuous group of three dimensional rotations of the entire coordinate system: from this follows the familiar result that total angular momentum is conserved. Thus, the eigenfunctions of this hamiltonian may form bases of the representations of the rotation group.

Group theoretic techniques have been used by Hirschfelder and Wigner[1], Curtiss, Hirschfelder and Adler[2], Curtiss and Adler[3], and Curtiss[4] to effect the separation of three rotational degrees of freedom from the corresponding N-particle Schroeding equation. The result is a set of coupled differential equations in the internal coordinates of the system.

In discussing the problem of the separation of the rotational degrees of freedom it is convenient to introduce the concept of a coordinate system whose origin is the center of mass of the N-particle system and which rotates so as to keep the N particles in a specified "standard configuration". The three degrees of freedom which are separated are the three Euler angles associated with the rotation which takes the original coordinate system into the standard configuration.

For a given system one particular set of internal coordinates may prove better suited to the problem than another. Moreover, for a given set of internal coordinates, the final coupled equations will differ depending on the definition of the standard configuration for the problem. Finally, different sets of internal coordinates together with different choices of the standard configuration may emphasize in dissimiliar ways any symmetry features of the problem, and perhaps suggest convenient methods of solving the final equations.

It is the purpose of this paper to develop the Schroedinger equation for the three particle problem H^+-H , in several sets of internal coordinates for each of two distinct choices of the standard configuration.

We begin by considering the full N-particle Schroedinger equation together with the formal separation of the translational and rotational degrees of freedom, and then specialize to the case of three particles.

I. Separation of the translational motion

The N-particle Schroedinger equation in a space fixed coordinate system is

$$-\frac{\hbar^2}{2}\sum_{n=1}^{N}\sum_{k=3}^{3}\frac{1}{m_n}\frac{\partial^2\Psi}{\partial x_{nk}^2} + V\Psi = E_T\Psi \qquad (I.1)$$

where V is the potential energy, m_n the mass of the n^{th} particle, E_T the total energy, and x_{nk} the position vector of the n^{th} particle in a space fixed coordinate system. We consider the N particles as members of two subsets, subset A and subset B. The particles in subset A are numbered 1,2,...a, while those in subset B are numbered a+1, a+2, ...N. The separation of the motion of the center of mass is carried out in two different sets of coordinates.

I.a. Center of mass coordinates. I

To separate the motion of the center of mass we employ the following sets of coordinates:

the three cartesian coordinates of the center of mass of the entire system,

$$Y_k = \sum_{n=1}^{N} m_n x_{nk} \Big/ \sum_{n=1}^{N} m_n$$

the three coordinates of the center of mass of subset A relative to the center of mass of subset B,

$$y_k = \frac{1}{M_A} \sum_{n=1}^{a} m_n x_{nk} - \frac{1}{M_B} \sum_{n=a+1}^{N} m_n x_{nk}$$

the coordinates of the first a-1 particles relative to the center of mass of subset A,

$$y_{nk} = x_{nk} - \frac{1}{M_A} \sum_{n'=1}^{a} m_{n'} x_{n'k} \quad (n=1, \ldots a-1)$$

and finally,

the coordinates of the particles of subset B relative to the center of mass of subset B,

$$y_{nk} = x_{nk} - \frac{1}{M_B}\sum_{n'=a+1}^{N} m_{n'} x_{n'k} \qquad (n=a+1,\ldots N-1)$$

These are illustrated in Figure 1. With this choice of coordinates the equation describing the relative motion of the entire system is

$$\left[-\frac{\hbar^2}{2}\sum_{n=1}^{a-1}\sum_{n'=1}^{a-1}\sum_{k=1}^{3}\frac{1}{m_n}\left(\delta_{nn'} - \frac{m_n}{M_A}\right)\frac{\partial^2}{\partial y_{nk}\partial y_{n'k}} - \frac{\hbar^2}{2}\sum_{n=a+1}^{N-1}\sum_{n'=a+1}^{N-1}\sum_{k=1}^{3}\frac{1}{m_n}\left(\delta_{nn'} - \frac{m_n}{M_B}\right)\frac{\partial^2}{\partial y_{nk}\partial y_{n'k}} - \frac{\hbar^2}{2\mu}\sum_{k=1}^{3}\frac{\partial^2}{\partial y_k^2} + V \right]\psi(y_k, y_{nk}) \qquad (I.2)$$

$$= E\,\psi(y_k, y_{nk})$$

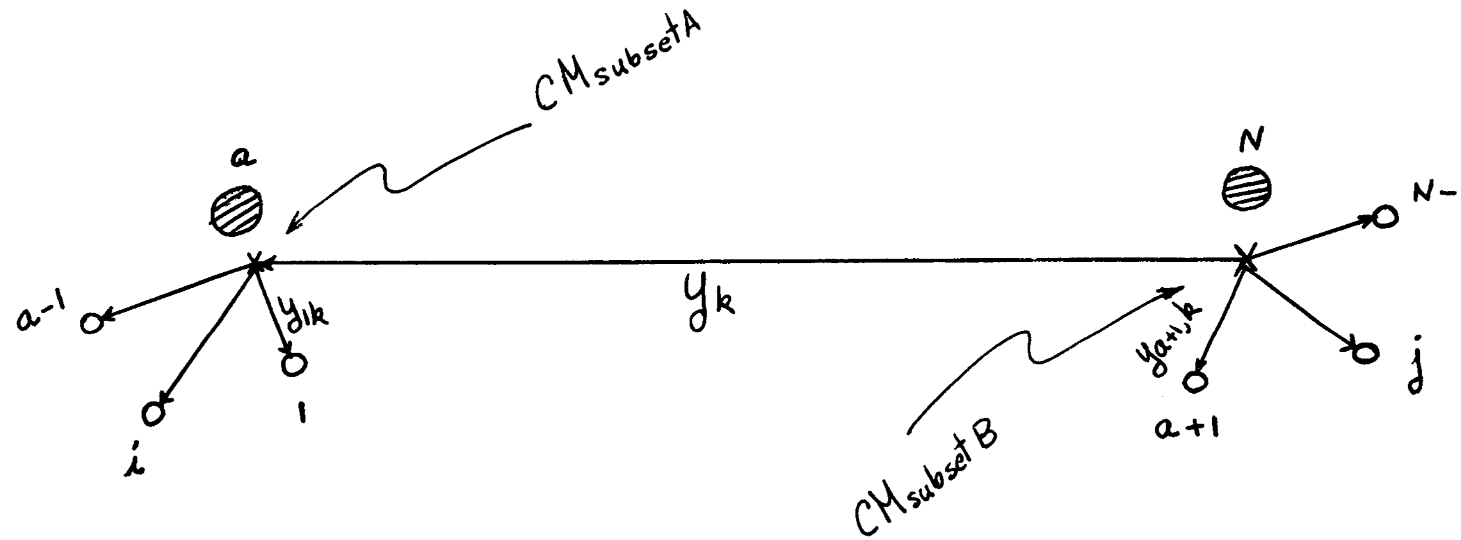

Figure 1

where $$M_A = \sum_{n=1}^{a} m_n$$

$$M_B = \sum_{n=a+1}^{N} m_n$$

and the quantity $\bar{\mu}$ is the reduced mass of the two subsets of particles. The energy E is the total energy less the translational contribution.

I.b. Center of mass coordinates. II

Consider next a second transformation, which we later associate with standard configuration II, in which the particles are again divided into two subsets and numbered 1,...a in subset A and a+1,...N in subset B.

To effect the separation of the center of mass we employ definitions of the coordinates which are slightly different from the previous choice. Specifically, these independent coordinates are:

the position of the center of mass of the entire system,

$$Y_k = \sum_{n=1}^{N} m_n X_{nk} \Big/ \sum_{n=1}^{N} m_n$$

the inter-particle vector,

$$y_k = x_{ak} - x_{Nk}$$

and

$$y_{nk} = x_{nk} - x_{ak}, (n=1,\dots a-1),$$

$$y_{nk} = x_{nk} - x_{Nk} , \quad (n=a+1,\dots N-1) \quad .$$

Thus, if a and N designate two nuclei, y_{nk} , $(n=1,\dots a-1)$, is seen to be the electronic vector of the n^{th} electron of subset A relative to nucleus a . A similar identification is made for the y_{nk}, $(n=a+1,\dots N-1)$, for subset B. These coordinates are illustrated in Figure 2.

The Schroedinger equation for the relative motion of the system, in the above coordinates, is

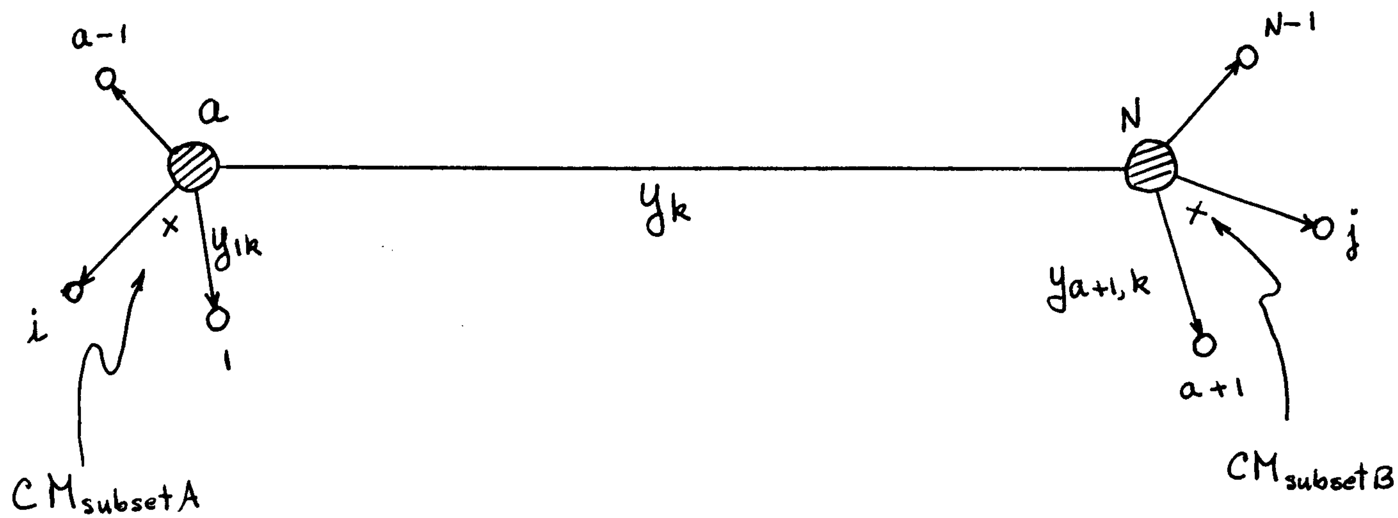

Figure 2

$$\left[\sum_{n=1}^{a-1} \sum_{n'=1}^{a-1} \sum_{k=1}^{3} \left(\frac{1}{m_a} + \frac{\delta_{nn'}}{m_n} \right) \frac{\partial^2}{\partial y_{nk} \partial y_{n'k}} \right.$$

$$+ \sum_{n=a+1}^{N-1} \sum_{n'=a+1}^{N-1} \sum_{k=1}^{3} \left(\frac{1}{m_N} + \frac{\delta_{nn'}}{m_n} \right) \frac{\partial^2}{\partial y_{nk} \partial y_{n'k}}$$

$$- \frac{2}{m_a} \sum_{n=1}^{a-1} \sum_{k=1}^{3} \frac{\partial^2}{\partial y_k \partial y_{nk}} + \frac{2}{m_N} \sum_{n=a+1}^{N-1} \sum_{k=1}^{3} \frac{\partial^2}{\partial y_k \partial y_{nk}}$$

$$\left. + \sum_{k=1}^{3} \left(\frac{1}{m_a} + \frac{1}{m_N} \right) \frac{\partial^2}{\partial y_k^2} \right] \psi(y_{nk}, y_k) \qquad \text{(I.3)}$$

$$= 2/\hbar^2 (E - V) \psi(y_{nk}, y_k)$$

where E is again the energy less the translational contribution.

It is evident that the separation based on the vector between nuclei (rather than the vector between the centers of mass of the two subsets) introduces cross terms in the expression for the kinetic energy.

II. Separation of the Rotational Coordinates

The problem of separating the rotational degrees of freedom from the N-particle Schroedinger is complicated by the question of how one specifies the orientation in space of an N-particle "non-rigid" body. As in the classical treatment of rigid bodies, we wish to define a set of Euler angles relating the "body-fixed" axes to the space-fixed axes. These angles can then be said to describe the orientation of the body relative to a space-fixed frame. For this purpose it is convenient to define a "standard configuration" of the N-particle system. A rotation $R(\alpha, \beta, \gamma)$ can then be defined as the rotation which takes the space-oriented center of mass coordinate system into coincidence with the body fixed system.

Since the hamiltonian commutes with the generators (the J_k) of the three dimensional rotation group, its eigenfunctions may form bases of the representations of the group. In particular, if ψ_μ^J is a wave function labeled by the total angular momentum J, and the space z-axis projection of the total angular momentum μ, a rotation R of the space fixed coordinates mixes the $2J+1$ degenerate states

$$U_R \psi_\mu^J = \sum_\rho \mathcal{D}^J(R)_{\rho\mu} \psi_\rho^J \qquad \text{(II.1)}$$

If R rotates the space fixed frame into the standard configuration, the values of the coordinates in the rotated frame,

y'_{nk} and y'_k, are given by

$$y'_{nk} = R^{-1} y_{nk}$$
$$y'_k = R^{-1} y_k \qquad \text{(II.2)}$$

We may define the standard configuration wave function as

$$\chi_\rho^J = \psi_\rho^J(y'_{nk}, y'_k) \qquad \text{(II.3)}$$

Making use of the identity

$$\psi_\rho^J(y'_{nk}, y'_k) = U_{R^{-1}} \psi_\rho^J(y_{nk}, y_k) \qquad \text{(II.4)}$$

it is easily seen that χ_ρ^J is given by

$$\chi_\rho^J = U_{R^{-1}} \psi_\rho^J(y_{nk}, y_k) \qquad \text{(II.5)}$$

Since a rotation R mixes the 2J+1 degenerate states χ_ρ^J, equation (II.1) can be used with equation (II.5) to give

$$\chi_\rho^J = \sum_\mu \mathcal{D}^J(R^{-1})_{\mu\rho} \psi_\mu^J = \sum_\mu \mathcal{D}^J(R)^*_{\rho\mu} \psi_\mu^J \qquad \text{(II.6)}$$

When use is made of the 'orthogonality' relation

$$\sum_{\rho} \mathcal{D}^{J}(R)_{\rho\mu'} \mathcal{D}^{J}(R)^{*}_{\rho\mu} = \delta_{\mu\mu'} \qquad \text{(II.7)}$$

it is possible to write ψ^{J}_{μ} as a sum of products of representation coefficients and functions involving only the 3N-6 internal coordinates

$$\psi^{J}_{\mu} = \sum_{\rho} \mathcal{D}^{J}(R)_{\rho\mu} \chi^{J}_{\rho} \qquad \text{(II.8)}$$

The two remaining tasks are first, to uniquely specify the rotation R, and second, to apply the hamiltonian of equations (I.2) and (I.3) to a wave function of the form given by equation (II.8).

We now define the two standard configurations associated with the two different center of mass coordinate systems, and consider explicitly the three particle problem, $H^{+} - H$, for which $a = 2$ and $N = 3$.

II.a. Standard Configuration I

Standard configuration I, associated with the center of mass coordinates used in obtaining equation (I.2), is defined by requiring that the vector between the centers of mass of the two subsets be along the z-axis and that particle 1 lie in the positive x-z half-plane. (See Figure 3) More precisely, we have

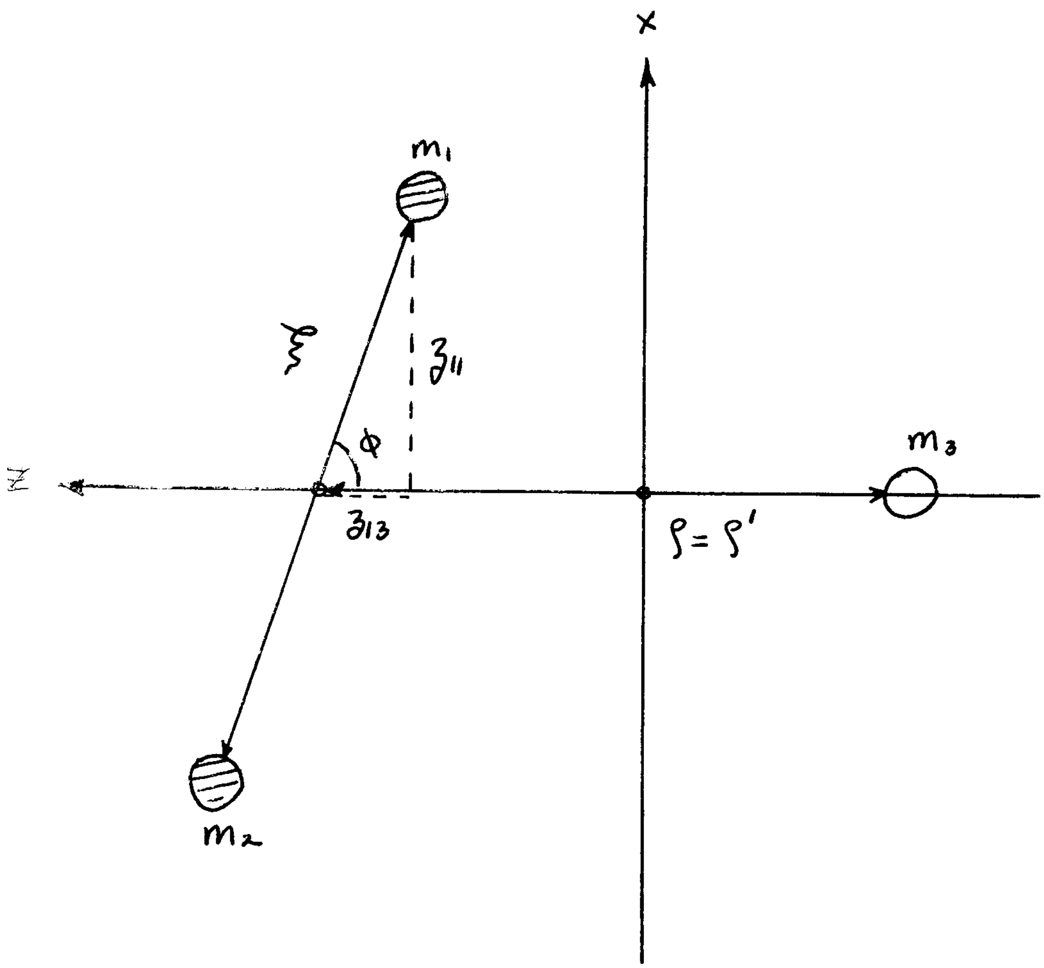

Figure 3

$$\sum_j R_{1j} y_j = 0$$

$$\sum_j R_{2j} y_j = 0 \qquad \text{(II.9)}$$

$$\sum_j R_{2j} y_{1j} = 0$$

The internal coordinates are then the cartesian coordinates in the rotated system, namely, (Figure 3)

$$\rho = \sum_j R_{3j} y_j \ , \qquad \text{(II.10)}$$

the distance between the two centers of mass, and

$$z_{1k} = \sum_j R_{kj} y_{1j} \ , \ (k=1,3) \qquad \text{(II.11)}$$

the coordinates of particle 1 relative to the center of mass of particles 1 and 2.

We choose to identify particles 1 and 2 as protons, and particle 3 as the electron. Then ρ is the distance between the electron and the center of mass of the two protons, while z_{11} and z_{13} are the coordinates of proton 1 relative to the center of mass of the proton system. Because of the specification of the rotation, (II.9), z_{12} is identically zero.

To carry out the transformation to the internal coordinates we must consider the effect of the hamiltonian of equation (II.2) operating on a wave function of the form

$$\psi_\mu^J = \sum_\rho \mathcal{D}^J(R)_{\rho\mu} \chi_\rho^J$$

Since the hamiltonian involves derivatives with respect to the "old variables", y_k and y_{1k}, we must evaluate expressions such as

$$\frac{\partial \psi_\mu^J(y_{1k}, y_k)}{\partial y_k} = \sum_\rho \frac{\partial \mathcal{D}^J(R)_{\rho\mu}}{\partial y_k} \chi_\rho^J + \sum_\rho \mathcal{D}^J(R)_{\rho\mu} \frac{\partial \chi_\rho^J}{\partial y_k} \tag{II.12}$$

$$\frac{\partial \psi_\mu^J(y_{1k}, y_k)}{\partial y_{1k}} = \sum_\rho \frac{\partial \mathcal{D}^J(R)_{\rho\mu}}{\partial y_{1k}} \chi_\rho^J + \sum_\rho \mathcal{D}^J(R)_{\rho\mu} \frac{\partial \chi_\rho^J}{\partial y_{1k}} \tag{II,13}$$

It is evident that this requires a knowledge of the derivatives of the "new variables", z_{11}, z_{13}, ρ, and the functions $D^J(R)_{\rho\mu}$ with respect to the y_k and y_{1k}. The actual evaluation of these derivatives is a lengthy operation and is described in detail elsewhere.[1,4,5] The final result is that the Schroedinger equation for the H^+-H problem can be written in terms of the internal coordinates ρ, z_{11}, and z_{13}, as

$$\left[K + \frac{\Lambda}{2\bar{\mu}\rho^2} + K_a + V\right] \chi_\rho^J(\rho, z_{11}, z_{13}) = E\, \chi_\rho^J(\rho, z_{11}, z_{13}) \tag{II.14}$$

where

$$K = -\frac{\hbar^2}{2\bar{\mu}\rho^2}\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial}{\partial\rho}\right) \tag{II.15}$$

$$K_a = -\frac{\hbar^2}{4m_p}\left\{\frac{\partial^2}{\partial z_{11}^2} + \frac{\partial^2}{\partial z_{13}^2} + \frac{1}{z_{11}}\frac{\partial}{\partial z_{11}} - \frac{\rho^2}{z_{11}^2}\right\} \tag{II.16}$$

$$\Lambda = -\tfrac{1}{2}\Big[\left(M_{\rho+1}^{(-)} - \hbar/i\,\lambda_-\sigma_-\right)\left(M_\rho^{(+)} - \hbar/i\,\lambda_+\sigma_+\right) + \left(M_{\rho-1}^{(+)} - \hbar/i\,\lambda_+\sigma_+\right)\left(M_\rho^{(-)} - \hbar/i\,\lambda_-\sigma_-\right)\Big] \tag{II.17}$$

The operators $M_\rho^{(\pm)}$ are defined by

$$M_\rho^{(\pm)} = \mp\frac{\hbar}{i}\left[\left(z_{13}\frac{\partial}{\partial z_{11}} - z_{11}\frac{\partial}{\partial z_{13}}\right) + \frac{z_{13}}{z_{11}}\rho\right] \tag{II.18}$$

and the numbers $\lambda_\pm(J,\rho)$ by

$$\lambda_\pm(J,\rho) = \left[J(J+1) - \rho(\rho\pm1)\right]^{1/2} \tag{II.19}$$

The operators $\sigma_{\pm}$ are raising and lowering operators on the index s ,

$$\sigma_{\pm} \chi_{\rho}^{J} = \chi_{\rho \pm 1}^{J} \tag{II.20}$$

and it is these operators which couple the equations.

II.b. Standard configuration II

Standard configuration II, which is associated with the definition of the center of mass coordinates leading to equation (I.3), is specified by requiring that the inter-particle vector be parallel to the z-axis, and that particle 1 lie in the positive x-z half-plane (Figure 4). Thus

$$\begin{aligned} \sum_j R_{1j} y_j &= \sum_j R_{2j} y_j = 0 \\ \sum_j R_{2j} y_{1j} &= 0 \end{aligned} \tag{II.21}$$

The internal coordinates of the problem are then (Figure 4),

$$\begin{aligned} \rho &= \sum_j R_{3j} y_j \\ z_{1k} &= \sum_j R_{kj} y_{1k} \text{ , } (k=1,3) \end{aligned} \tag{II.22}$$

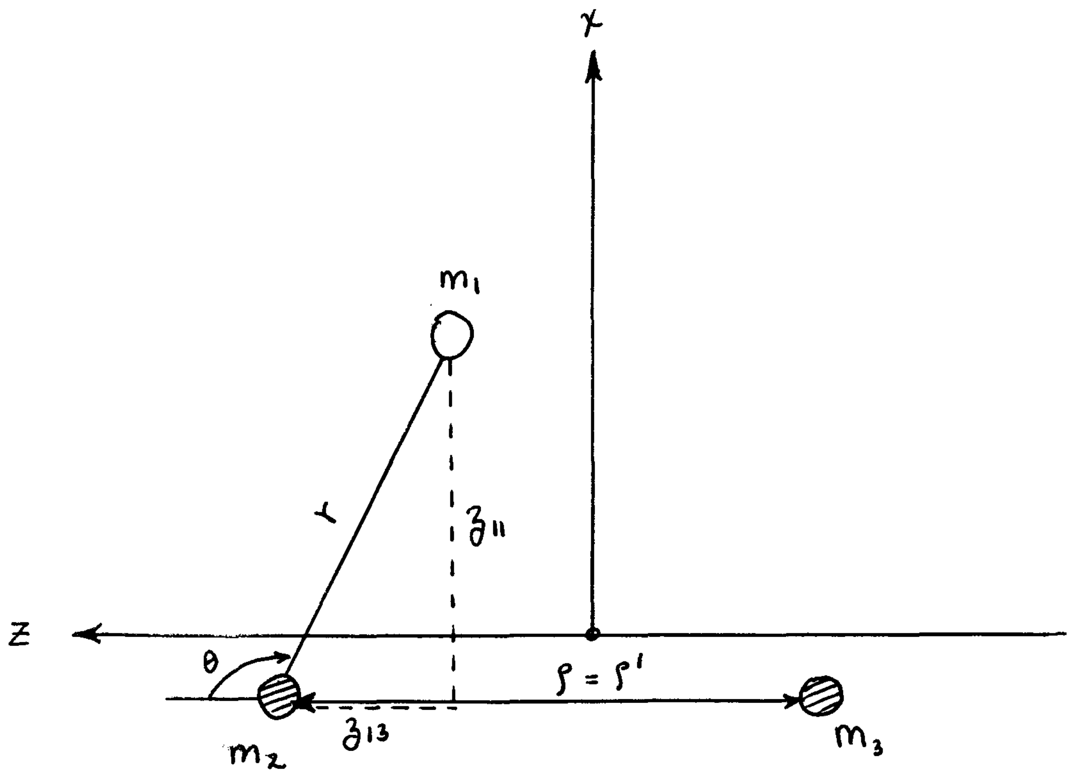

Figure 14

which correspond to the inter-proton distance and the electronic vector respectively, if particles 2 and 3 are the two protons and particle 1 the sole electron.

When the hamiltonian of equation (I.3) is applied to the wave function of equation (II.8), and use made of the expressions for the derivatives of the z_{1k}, ρ, R_{ij}, and $D(R)^J_{\rho\mu}$ as before, the final result is the Schroedinger equation for the system H^+-H in the internal coordinates ρ, z_{11}, z_{13}, corresponding to the second definition of the standard configuration. The resulting set of equations as obtained by Kouri[6] is

$$\left[K + K_a + \frac{\Lambda}{m_p} + V\right] \chi^J_\rho = E\,\chi^J_\rho \tag{II.23}$$

where

$$K = -\frac{\hbar^2}{m_p \rho^2} \frac{\partial}{\partial \rho}\left(\rho^2 \frac{\partial}{\partial \rho}\right) \tag{II.24}$$

$$K_a = -\frac{\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial z_{11}^2} + \frac{\partial^2}{\partial z_{13}^2} + \frac{1}{z_{11}}\frac{\partial}{\partial z_{11}} - \frac{\rho^2}{z_{11}^2}\right] \tag{II.25}$$

$$
\Lambda = -\hbar^2 \left[\begin{aligned}
& \frac{\zeta_{13}}{\rho^2 \zeta_{11}} \frac{\partial}{\partial \zeta_{11}} - \frac{2\zeta_{13}}{\rho^2} \frac{\partial}{\partial \zeta_{13}} + \frac{\zeta_{13}^2}{\rho^2} \frac{\partial^2}{\partial \zeta_{11}^2} - \frac{\zeta_{11}^2}{\rho^2} \frac{\partial}{\partial \zeta_{11}} \\
& - \frac{2\zeta_{13}\zeta_{11}}{\rho^2} \frac{\partial^2}{\partial \zeta_{11} \partial \zeta_{13}} + \frac{\zeta_{13}}{\rho^2} \left(\lambda_+ \sigma_+ - \lambda_- \sigma_- \right) \frac{\partial}{\partial \zeta_{11}} \\
& + \frac{\zeta_{11}^2}{\rho^2} \frac{\partial^2}{\partial \zeta_{13}^2} - \frac{\zeta_{11}}{\rho^2} \left(\lambda_+ \sigma_+ - \lambda_- \sigma_- \right) \frac{\partial}{\partial \zeta_{13}} \\
& - \frac{1}{2\rho^2} \left(\lambda_+^2 + \lambda_-^2 \right) - \frac{\zeta_{13}^2}{\rho^2 \zeta_{11}^2} s^2 + \frac{\zeta_{13}}{\rho \zeta_{11}} \frac{\partial}{\partial \zeta_{11}} - \frac{2}{\rho} \frac{\partial}{\partial \zeta_{11}} \\
& + \frac{\zeta_{13}}{\rho} \frac{\partial^2}{\partial \zeta_{11}^2} - \frac{\zeta_{11}}{\rho} \frac{\partial^2}{\partial \zeta_{11} \partial \zeta_{13}} + \frac{1}{2\rho} \left(\lambda_+ \sigma_+ - \lambda_- \sigma_- \right) \frac{\partial}{\partial \zeta_{11}} \\
& - \frac{s^2 \zeta_{13}^2}{\rho \zeta_{11}^2} - \frac{\partial^2}{\partial \rho \partial \zeta_{13}} - \Bigg\{ \left(\frac{\zeta_{13}}{\rho^2 \zeta_{11}} + \frac{1}{2\rho \zeta_{11}} \right) \left(\lambda_+ \sigma_+ - \lambda_- \sigma_- \right) \\
& + \left(\frac{s \zeta_{13}}{\rho^2 \zeta_{11}} + \frac{s}{2\rho \zeta_{11}} \right) \left(\lambda_+ \sigma_+ + \lambda_- \sigma_- \right) \Bigg\}
\end{aligned} \right] \tag{II.26}
$$

and μ is the reduced mass of the proton-electron pair.

Summarizing, we have utilized the translation invariant property of the hamiltonian of the system of N particles to remove three degrees of translational freedom from the problem. To do this we employed two different definitions of the center of mass coordinates.

Secondly, the invariance of the hamiltonian under the group of three dimensional rotations allowed the separation of three rotational degrees of freedom. Corresponding to the two definitions of the center of mass coordinates of relative motion, the y_k and y_{nk}, we specified two different rotations for the H^+-H problem which rotate the space fixed axes into the (two) standard configurations. The Euler angles associated with a given rotation change as the particles move so as to maintain the particles in the standard configuration. Thus, in the standard configuration the particles can execute only relative motion. The wave function can be written as a sum of products of representation coefficients $\overset{J}{D}(R)_{\rho\mu}$ and functions of the "internal" coordinates, the $\chi^J_\rho(\rho, \mathfrak{z}_{11}, \mathfrak{z}_{13})$

We arrive finally at two sets of coupled differential equations (II.14 and II.23) for the H^+-H system. In the next section we proceed to investigate various different sets of internal coordinates and compare the equations obtained from the two different standard configurations.

III. Standard Configuration I and the Internal Coordinates

This section is devoted to the development of the Schroedinger equation, as obtained using the first standard configuration, in three sets of internal coordinates. The formal definition of the new variables along with the expressions for the first derivatives with respect to the old variables are given for each transformation. The expressions for the second- and cross - derivatives are included in an appendix for convenience.

III.a. Internal Coordinates ρ', ξ, ϕ

We consider first a transformation to the set consisting of the inter proton distance ξ , the distance ρ' between the electron and the center of mass of the protons, and ϕ , the angle between these two. (Figure 3). Formally these coordinates are defined by the equations

$$\tan\phi = z_{11}/z_{13} \tag{III.1}$$

$$\xi = 2\sqrt{z_{11}^2 + z_{13}^2} \tag{III.2}$$

$$\rho' = \rho \tag{III.3}$$

With these definitions the derivatives with respect to the old variables become

$$\frac{\partial}{\partial z_{11}} = 2\left[\sin\phi \frac{\partial}{\partial \xi} + \frac{\cos\phi}{\xi}\frac{\partial}{\partial \phi}\right] \tag{III.4}$$

$$\frac{\partial}{\partial z_{13}} = 2\left[\cos\phi \frac{\partial}{\partial \xi} - \frac{\sin\phi}{\xi}\frac{\partial}{\partial \phi}\right] \tag{III.5}$$

$$\frac{\partial}{\partial \rho} = \frac{\partial}{\partial \rho'} \tag{III.6}$$

The Schroedinger equation in the internal coordinates ρ', ξ, and ϕ becomes

$$\left(K + H^{(0)}_{\rho\rho} + V\right)\chi^J_\rho + \sum_{\rho'} H^{(1)}_{\rho\rho'}\chi^J_{\rho'} = E\chi^J_\rho \tag{III.7}$$

where

$$K = -\frac{\hbar^2}{m_p}\left\{\frac{\partial^2}{\partial \xi^2} + \frac{2}{\xi}\frac{\partial}{\partial \xi}\right\} \tag{III.8}$$

$$H^{(0)}_{\rho\rho} = -\frac{\hbar^2(2m_p+m_e)}{4m_p m_e}\left[\frac{\partial^2}{\partial \rho'^2} + \frac{2}{\rho'}\frac{\partial}{\partial \rho'} + \frac{1}{\rho'^2}\left\{J(J+1) - 2\rho^2\right\} + \frac{\partial^2}{\partial \phi^2} + \cot\phi\frac{\partial}{\partial \phi} - \rho^2\csc^2\phi\right] \tag{III.9}$$

$$H^{(1)}_{\rho\rho} = -\frac{\hbar^2}{2m_p \xi^2}\left[\frac{\partial^2}{\partial\phi^2} + \cot\phi\frac{\partial}{\partial\phi} - \rho^2\csc^2\phi\right] \tag{III.10}$$

and

$$H^{(1)}_{\rho,\rho\pm1} = \mp\frac{\hbar^2(2m_p+m_e)}{4m_p m_e \rho'^2}\left\{\frac{\partial}{\partial\phi} \pm(\rho\pm1)\cot\phi\right\}\lambda_{\pm}(J,\rho) \tag{III.11}$$

The first two terms in equation (III.7) describe, respectively, the internal motion of the protons and the relative motion of the electron about the two protons. The term $H^{(1)}_{\rho\rho}$ corresponds to the internal motion of the three particles, and the $H^{(1)}_{\rho,\rho\pm1}$ is responsible for the coupling of the various rotational states.

III.b. Internal Coordinates r_1 , r_2 , and r_3

The second transformation is to the set of the three interparticle distances, r_1, r_2 and r_3. The following definitions apply (Figure 5).

$$r_1 = \rho'^2 + \bar{M}^2\xi^2 + 2\bar{M}\xi\rho'\cos\phi \tag{III.12}$$

$$r_2 = \rho'^2 + \bar{M}^2\xi^2 - 2\bar{M}\xi\rho'\cos\phi \tag{III.13}$$

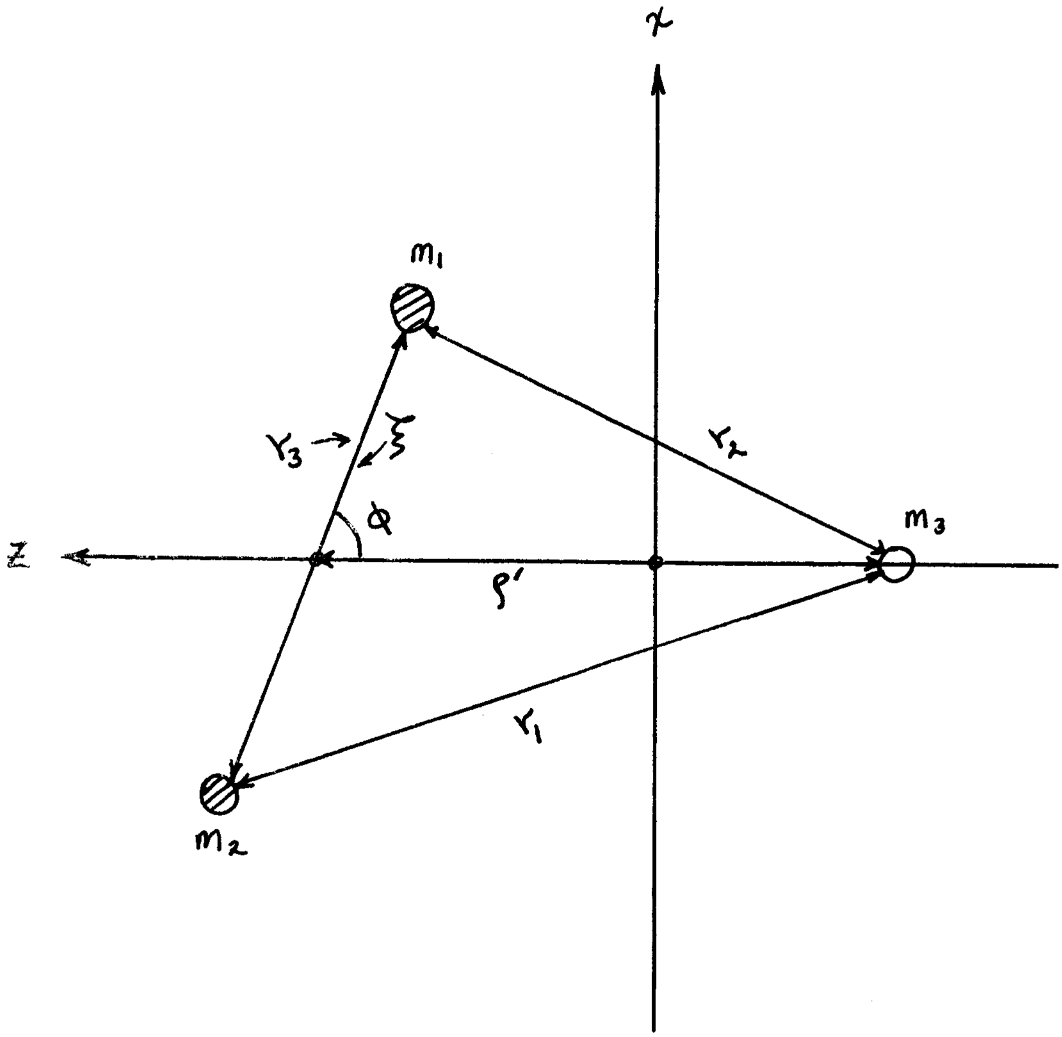

Figure 5

$$r_3 = \xi \tag{III.14}$$

with

$$M = \frac{m_1}{m_1 + m_2}$$

(= ½ when particles 1 and 2 are equivalent). The expressions for the derivatives may be shown to be

$$\frac{\partial}{\partial \xi} = \left\{ \frac{\bar{M}^2 r_3 + \bar{M} \rho' \cos\phi}{r_1} \frac{\partial}{\partial r_1} + \frac{\bar{M}^2 r_3 - \bar{M} \rho' \cos\phi}{r_2} \frac{\partial}{\partial r_2} + \frac{\partial}{\partial r_3} \right\} \tag{III.15}$$

$$\frac{\partial}{\partial \rho'} = \left\{ \frac{\rho' + \bar{M} r_3 \cos\phi}{r_1} \frac{\partial}{\partial r_1} + \frac{\rho' - \bar{M} r_3 \cos\phi}{r_2} \frac{\partial}{\partial r_2} \right\} \tag{III.16}$$

$$\frac{\partial}{\partial \phi} = \left\{ - \frac{\bar{M} r_3 \rho' \sin\phi}{r_1} \frac{\partial}{\partial r_1} + \frac{\bar{M} r_3 \rho' \sin\phi}{r_2} \frac{\partial}{\partial r_2} \right\} \tag{III.17}$$

After a moderate amount of algebra, the Schroedinger equation in the coordinates r_1, r_2, and r_3 may be written again in the form

$$\left(K + H^{(0)}_{\rho\rho} + V\right) \chi^J_\rho(r_1, r_2, r_3) + \sum_{\rho'} H^{(1)}_{\rho\rho'} \chi^J_{\rho'}(r_1, r_2, r_3) = E \chi^J_\rho(r_1, r_2, r_3) \tag{III.18}$$

where

$$K = -\frac{\hbar^2}{m_p}\frac{1}{r_3^2}\frac{\partial}{\partial r_3}\left(r_3^2\frac{\partial}{\partial r_3}\right) \tag{III.19}$$

$$H^{(0)}_{\rho\rho} = -\frac{\hbar^2}{2}\frac{2m_p+m_e}{2m_p m_e}\left[\frac{1}{r_1^2}\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial}{\partial r_1}\right) + \frac{1}{r_2^2}\frac{\partial}{\partial r_2}\left(r_2^2\frac{\partial}{\partial r_2}\right) + \right.$$

$$\left. + 2\frac{J(J+1)-2\rho^2}{\left(r_1^2+r_2^2-\frac{1}{2}r_3^2\right)} + \frac{r_1^2+r_2^2-r_3^2}{r_1 r_2}\frac{\partial^2}{\partial r_1 \partial r_2} - \frac{4r_3^2\rho^2}{B^2}\right] \tag{III.20}$$

$$H^{(0)}_{\rho\rho} = -\frac{\hbar^2}{m_p}\left[\frac{1}{4}\left\{\frac{1}{r_1^2}\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial}{\partial r_1}\right) + \frac{1}{r_2^2}\frac{\partial}{\partial r_2}\left(r_2^2\frac{\partial}{\partial r_2}\right) - \frac{r_1^2+r_2^2-r_3^2}{r_1 r_2}\right.\right.$$

$$- \frac{2\rho^2\left(r_1^2+r_2^2-\frac{1}{2}r_3^2\right)}{B^2} + \frac{r_1^2-r_2^2+r_3^2}{2r_1 r_3}\frac{\partial^2}{\partial r_1 \partial r_3}$$

$$\left.\left. + \frac{r_2^2+r_3^2-r_1^2}{2r_2 r_3}\frac{\partial^2}{\partial r_2 \partial r_3}\right]\right. \tag{III.21}$$

$$H^{(1)}_{\rho,\rho\pm 1} = \mp\frac{\hbar^2}{2}\frac{2m_p+m_e}{2m_p m_e}\frac{1}{\left(r_1^2+r_2^2-\frac{1}{2}r_3^2\right)}\left[-\frac{1}{4}B\left(\frac{1}{r_1}\frac{\partial}{\partial r_1} - \frac{1}{r_2}\frac{\partial}{\partial r_2}\right)\right.$$

$$\left. \pm(\rho\pm 1)\frac{r_1^2-r_2^2}{B}\right]\lambda_{\pm}(J,\rho) \tag{III.22}$$

with $$B = \left\{2\left(r_1^2 r_3^2 + r_1^2 r_2^2 + r_2^2 r_3^2\right) - \left(r_1^4 + r_2^4 + r_3^4\right)\right\}^{1/2}$$

This equation appears quite cumbersome and admits of little easy identification of its component parts. The set r_1, r_2, and r_3 has, however, the advantage of readily exhibiting any symmetries involving two or more of the coordinates. As the standard configuration upon which the form of this equation ultimately depends treats the two protons symmetrically we might consider the effect of interchanging the two protons. It is readily confirmed that all terms except the coupling term, $H^{(1)}_{s,s\pm 1}$, are invariant under this transformation.

III.c. Confocal elliptic coordinates

The equation in the three inter-particle distances immediately suggests a potentially more useful set of internal coordinates, namely the set of confocal elliptic coordinates. These coordinates are defined by

$$\lambda = \frac{r_1 + r_2}{r_3}$$

$$\mu = \frac{r_1 - r_2}{r_3} \qquad \text{(III.23)}$$

$$R = r_3$$

With these definitions the various first derivatives may be written

$$\frac{\partial}{\partial r_1} = \frac{1}{R}\left(\frac{\partial}{\partial\lambda} + \frac{\partial}{\partial\mu}\right) \tag{III.24}$$

$$\frac{\partial}{\partial r_2} = \frac{1}{R}\left(\frac{\partial}{\partial\lambda} - \frac{\partial}{\partial\mu}\right) \tag{III.25}$$

$$\frac{\partial}{\partial r_3} = -\frac{1}{R}\left(\lambda\frac{\partial}{\partial\lambda} + \mu\frac{\partial}{\partial\mu}\right) + \frac{\partial}{\partial R} \tag{III.26}$$

$$\frac{2}{r_1}\frac{\partial}{\partial r_1} + \frac{2}{r_2}\frac{\partial}{\partial r_2} = \frac{2}{R^2}\frac{4}{(\lambda^2-\mu^2)}\left(\lambda\frac{\partial}{\partial\lambda} - \mu\frac{\partial}{\partial\mu}\right) \tag{III.27}$$

The quantity B^2 is

$$B^2 = R^4(\lambda^2-1)(1-\mu^2) \tag{III.28}$$

Finally, the Schroedinger equation in confocal elliptic coordinates may be written

$$\left(K + H^{(0)}_{\rho\rho} + V\right)\chi^J_\rho(\lambda,\mu,R) + \sum_{\rho'} H^{(1)}_{\rho\rho'}\chi^J_{\rho'}(\lambda,\mu,R) = E\chi^J_\rho(\lambda,\mu,R) \tag{III.29}$$

where

$$K = -\frac{\hbar^2}{m_p}\frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) \tag{III.30}$$

$$\begin{aligned} H^{(0)}_{\rho\rho} = -\frac{\hbar^2(2m_p+m_e)}{m_p m_e R^2(\lambda^2-\mu^2)}\Bigg[&\frac{\partial}{\partial\lambda}\left\{(\lambda^2-1)\frac{\partial}{\partial\lambda}\right\}+\frac{\partial}{\partial\mu}\left\{(1-\mu^2)\frac{\partial}{\partial\mu}\right\} \\ &+(\lambda^2-\mu^2)\left\{\frac{J(J+1)-2\rho^2}{\lambda^2+\mu^2-1}-\frac{\rho^2}{(\lambda^2-1)(1-\mu^2)}\right\}\Bigg] \end{aligned} \tag{III.31}$$

$$H^{(1)}_{\rho\rho} = \frac{-\hbar^2}{m_p R^2(\lambda^2-\mu^2)}\left[\begin{aligned} &\frac{(\lambda^2+\mu^2-1)}{2}\left\{\frac{\partial}{\partial\lambda}\left[(\lambda^2-1)\frac{\partial}{\partial\lambda}\right]+\frac{\partial}{\partial\mu}\left[(1-\mu^2)\frac{\partial}{\partial\mu}\right]\right\} \\ &-(\lambda^2-\mu^2)\,\frac{\rho^2}{(\lambda^2-1)(1-\mu^2)} \\ &-2\lambda(\lambda^2-1)\left\{\frac{\partial}{\partial\lambda}+R\frac{\partial^2}{\partial\lambda\,\partial R}\right\}-2\mu(1-\mu^2)\left\{\frac{\partial}{\partial\mu}+R\frac{\partial^2}{\partial\mu\,\partial R}\right\} \end{aligned}\right] \tag{III.32}$$

$$\begin{aligned} H^{(1)}_{\rho,\rho\pm1} = \mp\frac{\hbar^2(2m_p+m_e)}{m_p m_e R^2(\lambda^2+\mu^2-1)\left[(\lambda^2-1)(1-\mu^2)\right]^{1/2}}\Bigg[&\frac{(\lambda^2-1)(1-\mu^2)}{\lambda^2-\mu^2}\times \\ &\left(\mu\frac{\partial}{\partial\lambda}-\lambda\frac{\partial}{\partial\mu}\right)\pm(\rho\pm1)\lambda\mu\Bigg]\lambda_{\pm}(J,\rho) \end{aligned} \tag{III.33}$$

IV. Standard Configuration II and the Internal Coordinates

In this section we develop the Schroedinger equation corresponding to the second definition of the standard configuration, equation (II.23), in three sets of internal coordinates, two of which are identical to the last two sets in the previous section. Thus the effect on the final equations of the different symmetrical treatments of the two protons may be noted. The presentation of results is similar to that in section III.

IV.a. Internal Coordinates r , ρ', θ

We begin with the transformation from the internal coordinates ρ , z_{11} , and z_{13} to the set of polar coordinates r , ρ' , and θ , defined by Figure 4.

$$\rho = \rho'$$

$$z_{11} = r \sin\theta \tag{IV.1}$$

$$z_{13} = r \cos\theta$$

The relevant first derivatives, in the new variables, are

$$\frac{\partial}{\partial z_{11}} = \sin\theta \frac{\partial}{\partial r} + \frac{\cos\theta}{r} \frac{\partial}{\partial \theta} \tag{IV.2}$$

$$\frac{\partial}{\partial z_{13}} = \cos\theta \frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial \theta} \tag{IV.3}$$

$$\frac{\partial}{\partial \rho} = \frac{\partial}{\partial \rho'} \tag{IV.4}$$

$$\frac{\partial^2}{\partial z_{11}^2} + \frac{\partial^2}{\partial z_{13}^2} = \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2} \tag{IV.5}$$

The Schroedinger equation in polar coordinates becomes[5,6]

$$\left(K + H^{(0)}_{ss} + V\right)\chi^J_s(r,\rho',\theta) + \sum_{s'} H^{(1)}_{ss'}\,\chi^J_{s'}(r,\rho',\theta) = E\,\chi^J_s(r,\rho',\theta) \tag{IV.6}$$

with

$$K = -\frac{\hbar^2}{m_p \rho'^2}\frac{\partial}{\partial \rho'}\left(\rho'^2 \frac{\partial}{\partial \rho'}\right) \tag{IV.7}$$

$$H^{(0)}_{ss} = -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) - \frac{s^2}{r^2\sin^2\theta}\right] \tag{IV.8}$$

$$H^{(1)}_{ss} = -\frac{\hbar^2}{m_p}\left[\begin{array}{l} -\cos\theta \dfrac{\partial^2}{\partial\rho'\partial r} + \dfrac{\sin\theta}{r}\dfrac{\partial^2}{\partial\rho'\partial\theta} - \dfrac{J(J+1)-2s^2}{\rho'^2} \\ + \dfrac{1}{r\rho'\sin\theta}\left(\dfrac{\partial}{\partial\theta} - s^2\cot\theta\right) - \dfrac{s^2}{\rho'^2\sin^2\theta} + \dfrac{1}{\rho'^2}\dfrac{\partial^2}{\partial\theta^2} \\ + \dfrac{1}{\rho'^2}\cot\theta\dfrac{\partial}{\partial\theta} + \dfrac{1}{\rho'}\left(\dfrac{\cos\theta}{r}\dfrac{\partial}{\partial\theta} + \sin\theta\dfrac{\partial}{\partial r}\right)\dfrac{\partial}{\partial\theta} \end{array}\right] \tag{IV.9}$$

$$H^{(1)}_{s,s\pm1} = \mp\frac{\hbar^2}{m_p}\left[\begin{array}{l} \dfrac{1}{2\rho'}\left(\sin\theta\dfrac{\partial}{\partial r} + \dfrac{\cos\theta}{r}\dfrac{\partial}{\partial\theta}\right) + \dfrac{1}{\rho'^2}\dfrac{\partial}{\partial\theta} \\ -\left(\dfrac{\cot\theta}{\rho'^2} + \dfrac{1}{2r\rho'\sin\theta}\right)(s\pm1) \end{array}\right]\lambda_\pm(J,s) \tag{IV.10}$$

The quantity μ has already been defined, and is the reduced mass of the proton-electron pair.

The term $H^{(o)}_{ss}$ in equation (IV.6) is clearly the spherical polar Laplacian for the electron with the term in Φ removed. This is related by a simple ratio of masses to the Born-Oppenheimer H_2^+ electronic hamiltonian.

The first term plus the centrifugal potential $-\dfrac{2J(J+1)}{m_p\,\rho'^2}$ is the radial equation in the absence of any potential. Finally, the terms $H^{(1)}_{s,s \pm 1}$ provide the coupling of the states of different s .

IV.b. Internal coordinates r_1, r_2, and r_3

The three inter-particle distances are defined by the equations

$$r_1 = r \tag{IV.11}$$

$$r_2^2 = r_3^2 + r_1^2 + 2r_1r_3 \cos\theta \tag{IV.12}$$

$$r_3 = \rho' \tag{IV.13}$$

To facilitate comparison of this next result with its counterpart in standard configuration I, (III.18), the above definitions correspond to an effective renumbering of the particles in standard configuration II. (Figure 6).

In view of the definition of the new variables, the first derivatives become

$$\frac{\partial}{\partial r} = \left[\frac{r_1 + r_3\cos\theta}{r_2}\frac{\partial}{\partial r_2} + \frac{\partial}{\partial r_1}\right] = \left[\frac{r_2^2 + r_1^2 - r_3^2}{2r_1r_2}\frac{\partial}{\partial r_2} + \frac{\partial}{\partial r_1}\right] \tag{IV.14}$$

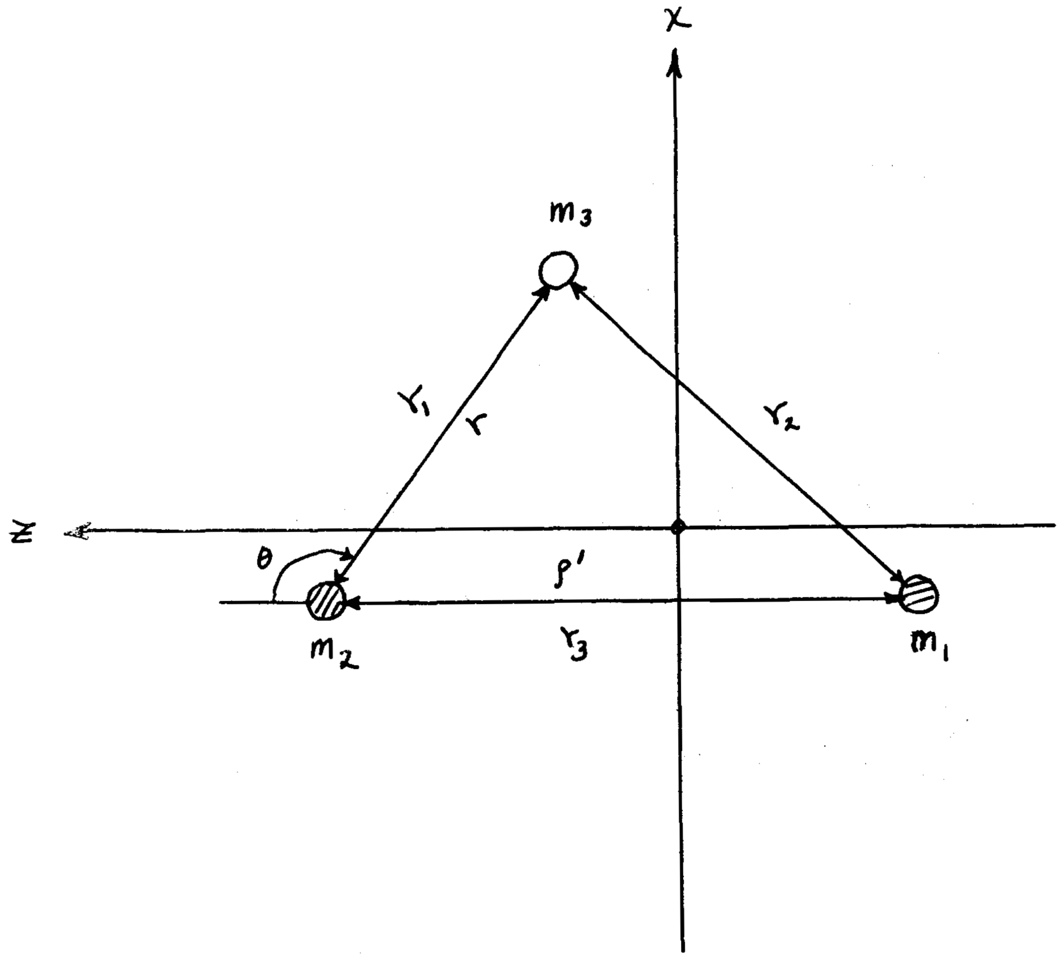

Figure 6

$$\frac{\partial}{\partial \rho'} = \left[\frac{\partial}{\partial r_3} + \frac{r_3 + r_1 \cos\theta}{r_2} \frac{\partial}{\partial r_2}\right] = \left[\frac{\partial}{\partial r_3} + \frac{r_2^2 + r_3^2 - r_1^2}{2 r_2 r_3} \frac{\partial}{\partial r_2}\right] \qquad \text{(IV.15)}$$

$$\frac{\partial}{\partial \theta} = - \frac{r_1 r_3 \sin\theta}{r_2} \frac{\partial}{\partial r_2} \qquad \text{(IV.16)}$$

The Schroedinger equation for H^+-H in r_1, r_2, and r_3 , and standard configuration II, may be shown to be

$$\left(K + H^{(0)}_{\rho\rho} + V\right) \chi^J_\rho (r_1, r_2, r_3) + \sum_{\rho'} H^{(1)}_{\rho\rho'} \chi^J_{\rho'}(r_1, r_2, r_3) = E \chi^J_\rho (r_1, r_2, r_3) \qquad \text{(IV.17)}$$

with

$$K = - \frac{\hbar^2}{m_p} \frac{1}{r_3^2} \frac{\partial}{\partial r_3}\left(r_3^2 \frac{\partial}{\partial r_3}\right) \qquad \text{(IV.18)}$$

$$H^{(0)}_{\rho\rho} = - \frac{\hbar^2}{2\mu} \left[\frac{1}{r_1^2} \frac{\partial}{\partial r_1}\left(r_1^2 \frac{\partial}{\partial r_1}\right) + \frac{1}{r_2^2} \frac{\partial}{\partial r_2}\left(r_2^2 \frac{\partial}{\partial r_2}\right) + \frac{r_1^2 + r_2^2 - r_3^2}{r_1 r_2} \frac{\partial^2}{\partial r_1 \partial r_2} - \frac{\rho^2}{r_1^2 B^2} \right] \qquad \text{(IV.19)}$$

$$H^{(1)}_{\rho\rho} = -\frac{\hbar^2}{m_p}\left[\frac{r_1^2+r_3^2-r_2^2}{2r_1r_3}\frac{\partial^2}{\partial r_1\partial r_3} - \frac{r_1^2+r_2^2-r_3^2}{2r_1r_2}\frac{\partial^2}{\partial r_1\partial r_2} + \frac{r_2^2+r_3^2-r_1^2}{2r_2r_3}\frac{\partial^2}{\partial r_2\partial r_3} - \frac{J(J+1)-2\rho^2}{r_3^2} + \frac{2\rho^2(r_3^2-r_2^2-r_1^2)}{B^2}\right] \tag{IV.20}$$

$$H^{(1)}_{\rho,\rho\pm1} = \mp\frac{\hbar^2}{m_p}\left[B r_1\frac{\partial}{\partial r_1} - 2r_1^2 B\frac{1}{r_2}\frac{\partial}{\partial r_2} - \frac{1}{B}\left\{\frac{r_2^2-r_1^2-r_3^2+4r_1^2r_3^4}{4r_1^2r_3^4}\right\}(\rho\pm1)\right]\lambda_\pm(J,\rho) \tag{IV.21}$$

The quantity B is defined in connection with equation (III.18).

Again it is easily verified that all terms except the coupling terms possess the property of being invariant under proton interchange.

IV.c. The confocal elliptic coordinates

Since the particles are now numbered identically in the two standard configurations, the final transformation, into the confocal elliptic system, has already been defined (III.23). The expressions for the first derivatives remain the same and a little work shows the Schroedinger equation in confocal elliptic coordinates and standard configuration II to be

$$\left(K + H^{(0)}_{\rho\rho} + V\right)\chi^J_\rho(\lambda,\mu,R) + \sum_{\rho'} H^{(1)}_{\rho\rho'}\chi^J_{\rho'}(\lambda,\mu,R) = E\,\chi^J_\rho(\lambda,\mu,R) \qquad \text{(IV.22)}$$

with

$$K = -\frac{\hbar^2}{m_p}\frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) \qquad \text{(IV.23)}$$

$$H^{(0)}_{\rho\rho} = -\frac{2\hbar^2}{\mu R^2(\lambda^2-\mu^2)}\left[\frac{\partial}{\partial\lambda}\left\{(\lambda^2-1)\frac{\partial}{\partial\lambda}\right\}\right.$$

$$\left. + \frac{\partial}{\partial\mu}\left\{(1-\mu^2)\frac{\partial}{\partial\mu}\right\} - \frac{\rho^2(\lambda^2-\mu^2)}{(\lambda^2-1)(1-\mu^2)}\right] \qquad \text{(IV.24)}$$

$$H^{(1)}_{\rho\rho} = \frac{-\hbar^2}{m_\rho R^2(\lambda^2-\mu^2)} \left[\begin{aligned} &(\lambda^2+\mu^2-2)\left\{(\lambda^2-1)\frac{\partial^2}{\partial\lambda^2} + (1-\mu^2)\frac{\partial^2}{\partial\mu^2}\right\} \\ &-2\lambda(1-\mu^2)\frac{\partial}{\partial\lambda} - 2\mu(\lambda^2-1)\frac{\partial}{\partial\mu} \\ &-2\lambda\mu(\lambda^2-\mu^2-1)\frac{\partial^2}{\partial\lambda\partial\mu} \\ &+2R\left\{\lambda(1-\mu^2)\frac{\partial^2}{\partial\lambda\partial R} + \mu(\lambda^2-1)\frac{\partial^2}{\partial\mu\partial R}\right\} \\ &-(\lambda^2-\mu^2)\left[J(J+1)-2\rho^2\right] \\ &\qquad - \frac{\rho^2(\lambda^2-\mu^2)(\lambda^2+\mu^2-2)}{(\lambda^2-1)(1-\mu^2)} \end{aligned} \right] \tag{IV.25}$$

$$H^{(1)}_{\rho,\rho\pm1} = \frac{\mp\hbar^2}{m_\rho R^2(\lambda^2-\mu^2)} \left[\frac{1}{2}\left[(\lambda^2-1)(1-\mu^2)\right]^{1/2}\left\{(3\mu-\lambda)\frac{\partial}{\partial\lambda} - (3\lambda-\mu)\frac{\partial}{\partial\mu}\right\} - \frac{\lambda^3(\lambda-2\mu)+\mu^3(\mu+2\lambda)}{\left[(\lambda^2-1)(1-\mu^2)\right]^{1/2}}(\rho\pm1)\right]\lambda_\pm(J,\rho) \tag{IV.26}$$

V. Summary

The translational and rotational invariance of the hamiltonian for the $H^+ - H$ system has been employed to separate three translational and three rotational degrees of freedom. In utilizing the rotational invariance we defined the rotation which carries the space fixed frame into a body fixed frame in two different ways. This defined two standard configurations of the three particles. Both definitions treated the protons symmetrically. A consequence of this symmetry is explicitly evident in equations III.18 and IV.17. It is easily shown that these equations are, except for the coupling terms, completely symmetric in the coordinates r_1 and r_2.

Sections III and IV are devoted to the development of the Schroedinger equation for $H^+ - H$ in three different sets of internal coordinates and a particular choice of the standard configuration. The resulting six sets of equations may each be written in terms of five operators, two of which exhibit explicitly the coupling of the various rotational states. The other three represent the electronic motion about the stationary nuclei, the motion of the nuclei, and the internal motion of the entire three particles.

APPENDIX

A.III.a

$$\left(z_{13}\frac{\partial}{\partial z_{11}} - z_{11}\frac{\partial}{\partial z_{13}}\right) = \left[\begin{array}{l} \xi\cos\phi\left(\sin\phi\dfrac{\partial}{\partial\xi} + \dfrac{\cos\phi}{\xi}\dfrac{\partial}{\partial\phi}\right) \\ \\ -\,\xi\sin\phi\left(\cos\phi\dfrac{\partial}{\partial\xi} - \dfrac{\sin\phi}{\xi}\dfrac{\partial}{\partial\phi}\right) \end{array}\right]$$

A.III.b

$$J = \frac{\partial(r_1, r_2, r_3)}{\partial(\xi, \rho'\phi)} = \begin{pmatrix} \dfrac{\bar{M}^2 r_3 + \bar{M}\rho'\cos\phi}{r_1} & \dfrac{\rho' + \bar{M} r_3\cos\phi}{r_1} & -\dfrac{\bar{M} r_3\rho'\sin\phi}{r_1} \\ \dfrac{\bar{M}^2 r_3 - \bar{M}\rho'\cos\phi}{r_2} & \dfrac{\rho' - \bar{M} r_3\cos\phi}{r_2} & \dfrac{\bar{M} r_3\rho'\sin\phi}{r_2} \\ 1 & 0 & 0 \end{pmatrix}$$

$$J = \frac{2\bar{M} r_3 \rho'^2 \sin\phi}{r_1 r_2}$$

$$\frac{\partial(\Xi, \rho', \phi)}{\partial(r_1, r_2, r_3)} = \begin{pmatrix} 0 & 0 & 1 \\[2ex] \dfrac{r_1}{2\rho'} & \dfrac{r_2}{2\rho'} & -\dfrac{\bar{M}^2 r_3}{\rho'} \\[2ex] \dfrac{r_1(\bar{M} r_3 \cos\phi - \rho')}{2\bar{M} r_3 \rho'^2 \sin\phi} & \dfrac{r_2(\bar{M} r_3 \cos\phi + \rho')}{2\bar{M} r_3 \rho'^2 \sin\phi} & \dfrac{(\rho'^2 - \bar{M}^2 r_3^2)\cos\phi}{r_3 \rho'^2 \sin\phi} \end{pmatrix}$$

$$\frac{\partial^2}{\partial \rho'^2} = \left[\begin{aligned} & \frac{\bar{M}^2 r_3^2 \sin^2\phi}{r_1^2} \frac{1}{r_1} \frac{\partial}{\partial r_1} + \frac{\bar{M}^2 r_3^2 \sin^2\phi}{r_2^2} \frac{1}{r_2} \frac{\partial}{\partial r_2} \\ & \left(1 - \frac{\bar{M}^2 r_3^2 \sin^2\phi}{r_1^2}\right) \frac{\partial^2}{\partial r_1^2} + \left(1 - \frac{\bar{M}^2 r_3^2 \sin^2\phi}{r_2^2}\right) \frac{\partial^2}{\partial r_2^2} \\ & + \left(\frac{\rho'^2 - \bar{M}^2 r_3^2 \cos^2\phi}{r_1 r_2}\right) \frac{\partial^2}{\partial r_1 \partial r_2} \end{aligned} \right]$$

$$\frac{\partial^2}{\partial\phi^2} = \left[\bar{M}^2 r_3^2 \rho'^2 \sin^2\phi \left\{ \frac{1}{r_1^2}\left(\frac{\partial^2}{\partial r_1^2} - \frac{1}{r_1}\frac{\partial}{\partial r_1}\right) + \frac{1}{r_2^2}\left(\frac{\partial^2}{\partial r_2^2} - \frac{1}{r_2}\frac{\partial}{\partial r_2}\right) - \frac{2}{r_1 r_2}\frac{\partial^2}{\partial r_1 \partial r_2} \right\} - \bar{M} r_3 \rho' \cos\phi \left(\frac{1}{r_1}\frac{\partial}{\partial r_1} - \frac{1}{r_2}\frac{\partial}{\partial r_2}\right) \right]$$

$$\frac{\partial^2}{\partial\xi^2} = \left[\bar{M}^2 \rho'^2 \sin^2\phi \left(\frac{1}{r_1^3}\frac{\partial}{\partial r_1} + \frac{1}{r_2^3}\frac{\partial}{\partial r_2}\right) + \frac{\partial^2}{\partial r_3^2} + \left(\bar{M}^2 - \frac{\bar{M}^2\rho'^2 \sin^2\phi}{r_1^2}\right)\frac{\partial^2}{\partial r_1^2} + \left(\bar{M}^2 - \frac{\bar{M}^2\rho'^2\sin^2\phi}{r_2^2}\right)\frac{\partial^2}{\partial r_2^2} + 2\,\frac{\bar{M}^4 r_3^2 - \bar{M}^2\rho'^2\cos^2\phi}{r_1 r_2}\,\frac{\partial^2}{\partial r_1 \partial r_2} + 2\,\frac{\bar{M}^2 r_3 - \bar{M}\rho'\cos\phi}{r_2}\,\frac{\partial^2}{\partial r_2 \partial r_3} + 2\,\frac{\bar{M}^2 r_3 + \bar{M}\rho'\cos\phi}{r_1}\,\frac{\partial^2}{\partial r_1 \partial r_3} \right]$$

A.III.c.

$$\frac{\partial^2}{\partial r_1 \partial r_2} = \frac{1}{R^2}\left(\frac{\partial^2}{\partial \lambda^2} - \frac{\partial^2}{\partial \mu^2}\right)$$

$$\frac{\partial^2}{\partial r_1 \partial r_3} = -\frac{1}{R^2}\left[\lambda \frac{\partial^2}{\partial \lambda^2} + \mu \frac{\partial^2}{\partial \mu^2} + \frac{\partial}{\partial \lambda} + \frac{\partial}{\partial \mu} + (\mu + \lambda)\frac{\partial^2}{\partial \lambda \partial \mu} + \frac{1}{R}\left(\frac{\partial^2}{\partial \lambda \partial R} + \frac{\partial^2}{\partial \mu \partial R}\right)\right]$$

A.IV.a.

$$\frac{\partial^2}{\partial z_{11}^2} = \left[\sin^2\theta \frac{\partial^2}{\partial r^2} + \frac{\cos^2\theta}{r^2}\frac{\partial^2}{\partial \theta^2} + \frac{\cos^2\theta}{r}\frac{\partial}{\partial r} + \frac{2\cos\theta\sin\theta}{r}\frac{\partial^2}{\partial \theta \partial r} - \frac{\sin\theta\cos\theta}{r^2}\frac{\partial}{\partial \theta}\right]$$

$$\frac{\partial^2}{\partial z_{13}^2} = \left[\cos^2\theta \frac{\partial^2}{\partial r^2} + \frac{\sin^2\theta}{r^2}\frac{\partial^2}{\partial \theta^2} - \frac{2\cos\theta\sin\theta}{r}\frac{\partial^2}{\partial \theta \partial r} + \frac{\sin\theta\cos\theta}{r^2}\frac{\partial}{\partial \theta} + \frac{\sin^2\theta}{r}\frac{\partial}{\partial r}\right]$$

A.IV.b.

$$J = \frac{\partial(r_1, r_2, r_3)}{\partial(r, \rho', \theta)} = \begin{pmatrix} 1 & 0 & 0 \\ \dfrac{r + \rho' \cos\theta}{r_2} & \dfrac{\rho' + r\cos\theta}{r_2} & -\dfrac{r\rho' \sin\theta}{r_2} \\ 0 & 1 & 0 \end{pmatrix}$$

$$J = \frac{r_1 r_3 \sin\theta}{r_2}$$

$$\frac{\partial(r, \rho', \theta)}{\partial(r_1, r_2, r_3)} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ \dfrac{r_1 + r_3\cos\theta}{r_1 r_3 \sin\theta} & -\dfrac{r_2}{r_1 r_3 \sin\theta} & \dfrac{r_3 + r_1 \cos\theta}{r_1 r_3 \sin\theta} \end{pmatrix}$$

$$\frac{\partial^2}{\partial\theta^2} = \frac{r_1^2 r_3^2 \sin\theta}{r_2} \left(\frac{\sin\theta}{r_2} \frac{\partial^2}{\partial r_2^2} - \frac{\sin\theta}{r_2} \frac{1}{r_2} \frac{\partial}{\partial r_2} \right.$$

$$\left. - \frac{\cos\theta}{r_1 r_3 \sin\theta} \frac{\partial}{\partial r_2} \right)$$

$$\frac{\partial^2}{\partial r^2} = \left[\left(1+\frac{r_3^2\cos^2\theta - r_3^2}{r_2^2}\right)\left(\frac{\partial^2}{\partial r_2^2} - \frac{1}{r_2}\frac{\partial}{\partial r_2}\right) + \frac{\partial^2}{\partial r_1^2}\right.$$

$$\left. + \frac{r_2^2 + r_1^2 - r_3^2}{r_1 r_2}\frac{\partial^2}{\partial r_1 \partial r_2} + \frac{1}{r_2}\frac{\partial}{\partial r_2}\right]$$

$$\frac{\partial^2}{\partial \rho \partial r} = \left[\begin{array}{l} \dfrac{r_1 + r_3\cos\theta}{r_2}\dfrac{\partial^2}{\partial r_2 \partial r_3} + \dfrac{r_3 + r_1\cos\theta}{r_2}\dfrac{\partial^2}{\partial r_1 \partial r_2} \\ + \dfrac{\partial^2}{\partial r_1 \partial r_3} + \dfrac{\cos\theta}{r_2}\dfrac{\partial}{\partial r_2} \\ + \left(\dfrac{r_3 + r_1\cos\theta}{r_2}\right)^2\left(\dfrac{\partial^2}{\partial r_2^2} - \dfrac{1}{r_2}\dfrac{\partial}{\partial r_2}\right) \end{array}\right]$$

$$\frac{\partial^2}{\partial \rho \partial \theta} = \left[-\frac{r_1\sin\theta}{r_2}\frac{\partial}{\partial r_2} - \frac{r_1 r_3 \sin\theta}{r_2}\frac{\partial^2}{\partial r_2 \partial r_3}\right.$$

$$\left. - \frac{(r_3 + r_1\cos\theta)\, r_1 r_3 \sin\theta}{r_2^2}\left(\frac{\partial^2}{\partial r_2^2} - \frac{1}{r_2}\frac{\partial}{\partial r_2}\right)\right]$$

$$\frac{\partial^2}{\partial r \partial \theta} = \left[-\frac{(r_1 + r_3\cos\theta)\, r_1 r_3 \sin\theta}{r_2^2}\left(\frac{\partial^2}{\partial r_2^2} - \frac{1}{r_2}\frac{\partial}{\partial r_2}\right)\right.$$

$$\left. - \frac{r_1 r_3 \sin\theta}{r_2}\frac{\partial^2}{\partial r_1 \partial r_2} - \frac{r_3\sin\theta}{r_2}\frac{\partial}{\partial r_2}\right]$$

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